

# Normal coordinate analysis and quantum chemical study of tris(*p*-fluorophenyl)antimony di(*N*-phenylglycinate)

$[(p\text{-FC}_6\text{H}_4)_3\text{Sb}(\text{O}_2\text{CCH}_2\text{NHC}_6\text{H}_5)_2]$

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**Abstract.** A complete normal coordinate analysis was performed by two different methods: a classical Wilson's G-F matrix method and the semi-empirical molecular orbital PM3 method, for a five coordinate tris(*p*-fluorophenyl)antimony di(*N*-phenylglycinate)  $[(p\text{-FC}_6\text{H}_4)_3\text{Sb}(\text{O}_2\text{CCH}_2\text{NHC}_6\text{H}_5)_2]$ , known to be an *in vitro* antitumour molecule.

**Keywords.** FT-IR spectra; tris(*p*-fluorophenyl)antimony di(*N*-phenylglycinate); normal coordinate analysis; semi-empirical.

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## 1. Introduction

In most of the organoantimony (V) compounds, the coordination number of antimony atom is five, whereas in some cases it may be six [1,2] or seven [3,4] also. The stretching vibrational frequencies of carbonyl groups in organoantimony carboxylates play a vital role in the determination of their structures. If there are interactions between the antimony atom and the carbonyl oxygen atoms, the asymmetric absorption vibrational frequencies  $\nu_{\text{asym}}$  of carbonyl groups decrease, while the symmetric absorption vibrational frequencies  $\nu_{\text{sym}}$  increase, and hence the difference between these two frequencies  $\Delta\nu$  also decreases [5,6]. The title compound tris(*p*-fluorophenyl)antimony di(*N*-phenylglycinate)  $[(p\text{-FC}_6\text{H}_4)_3\text{Sb}(\text{O}_2\text{CCH}_2\text{NHC}_6\text{H}_5)_2]$  shows a moderate value of  $\Delta\nu$  which indicates that there may be intermediate interaction between the antimony atom and the carbonyl oxygen atoms. In this study, experimental FT-IR is compared with theoretical frequencies obtained by normal

coordinate analysis using two different methods: a classical mechanics Wilson G-F matrix method and the semi-empirical quantum chemical molecular orbital PM3 method. Thus the advantages of the evaluation of both the methods, is useful for obtaining a reliable assignment of the vibrational spectra. To the best of our knowledge, the work on the normal coordinate analysis, for the title compound is yet to be reported. The compound is reported to possess antitumour activity against three cancer cells, viz. KB cells, Bel-7402 cells and HCT-8 cells *in vitro* [7].

## 2. Theory

The Wilson's G-F matrix method [8] with Urey-Bradley [9] force field has been used to evaluate the normal modes.

These are given by the eigenvalues  $\lambda$  of the secular equation  $GFL = \lambda L$ , where  $\lambda = 4\pi^2c^2\nu^2$ . The potential energy distribution (PED) in the  $j$ th internal coordinate for the  $i$ th normal mode is given by  $\text{PED} = \frac{L_{ji}^*L_{ji}F_{ji}}{\lambda_i}$ .

## 3. Experimental

### 3.1 Structure

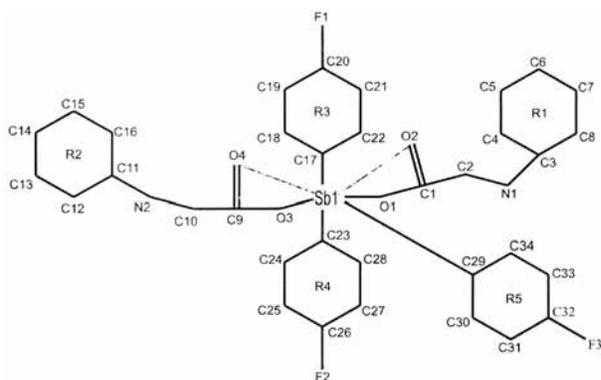
The crystal structure of the title compound tris(*p*-fluorophenyl)antimony di(*N*-phenylglycinate)  $[(p\text{-FC}_6\text{H}_4)_3\text{Sb}(\text{O}_2\text{CCH}_2\text{NHC}_6\text{H}_5)_2]$  is taken from the work of Yu *et al* [7]. The model molecular structure of the compound is given in figure 1.

### 3.2 FT-IR spectra

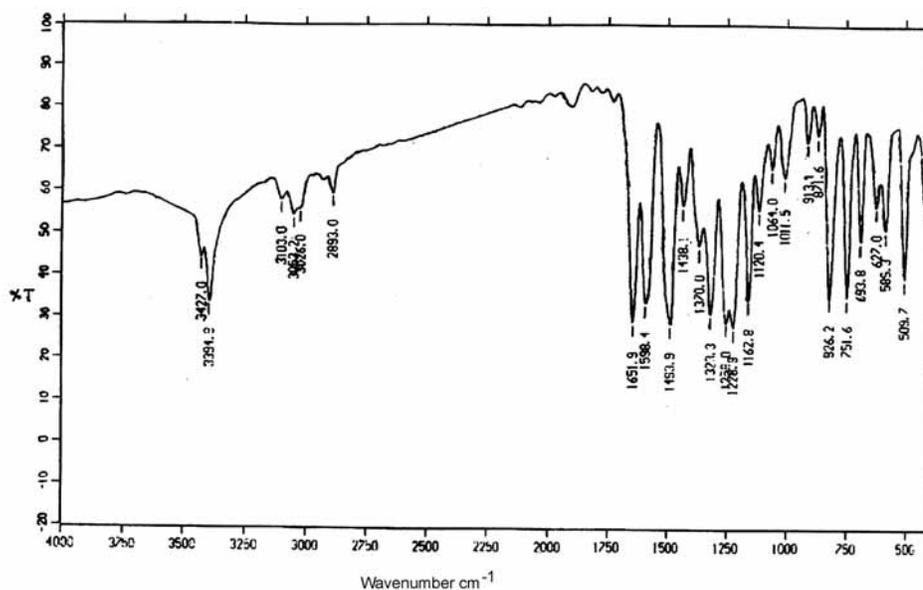
The FT-IR spectra, given in figure 2, were recorded on a Bruker Equinox 55 spectrophotometer, in KBr discs, in the range 4000–400  $\text{cm}^{-1}$ . X-ray data of the title compound has been taken from the CCDC [10].

## 4. Results and discussion

Normal coordinate calculations were performed using the program developed by Shimanouchi [11] based on Wilson's G-F matrix method [8]. We have used Urey-Bradley force field [9] in our calculations, which takes into account both bonded and non-bonded interactions and internal tensions. For the assignments, the force constants were initially transferred from our earlier work and literature [12–17] and were further refined by least square fit method to provide best match with the observed FT-IR spectra. (All the force constants can be made available on request from the corresponding author.)



**Figure 1.** Model molecular structure of tris(*p*-fluorophenyl)antimony di(*N*-phenylglycinate) [(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sb(O<sub>2</sub>CCH<sub>2</sub>NHC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>].



**Figure 2.** FTIR spectra of tris(*p*-fluorophenyl)antimony di(*N*-phenylglycinate) [(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sb(O<sub>2</sub>CCH<sub>2</sub>NHC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>].

In the assignment of the normal modes, as given in table 1, only the dominant potential energy distributions (PEDs) are considered. Identification with the experimental data has been made on the basis of potential energy distribution, line profile, line intensities and the presence/absence of a given mode in similar molecules [12,18,19].

Semi-empirical calculations were performed by Mopac 2007 software using PM3 method [20]. The observed frequencies agree with the calculated ones within 10 cm<sup>-1</sup>. (Complete computational details can be had from the corresponding author.)

**Table 1.** Calculated and observed vibrational modes.

Calculated frequency (cm <sup>-1</sup> )		Observed frequency (cm <sup>-1</sup> )	Assignment (% potential energy distribution) (PED)
Wilson G-F	PM3		
-	3285	3427(m)	$\nu(\text{N-H})\text{adj-R1}(\text{PM3})$
-	3283	3395(s)	$\nu(\text{N-H})\text{adj-R2}(\text{PM3})$
-	3006	3103(w)	$\nu(\text{C-H})\text{R1-sym} + \nu(\text{C-H})\text{R2-sym}(\text{PM3})$
-	3000	3053(m)	$\nu(\text{C-H})\text{R3-sym}(\text{PM3})$
-	2998	3026(w sh)	$\nu(\text{C-H})\text{R1-asym}(\text{PM3})$
-	2997	2893(m)	$\nu(\text{C-H})\text{R4-sym}(\text{PM3}) + \nu(\text{C-H})\text{R3-asym}(\text{PM3})$
1660	1632	1652(vs)	$\nu(\text{O=C}) (64) + \nu(\text{C-O})\text{adj-Sb} (20) + \nu(\text{C-C})\text{-out-of-R} (14) + \nu(\text{C-F})\text{R5}(\text{PM3})$
1590	1616	1598(s)	$\nu(\text{O=C}) (76) + \nu(\text{C-O}) (26) + \nu(\text{C-C})\text{R5-sym}(\text{PM3}) + \nu(\text{C-F})\text{R5}(\text{PM3})$
1495	1494	1494(s)	$\nu(\text{C-C})\text{R5-sym} (96) + \phi(\text{C-C-H})\text{R5}(\text{PM3})$
1428	1421	1438(w)	$\nu(\text{C-C})\text{R5-sym} (92) + \nu(\text{C-F})\text{R5}(\text{PM3}) + \phi(\text{C-C-H})\text{R5}(\text{PM3})$
1376	1361	1370(m)	$\nu(\text{C-C})\text{R2} (98) + \nu(\text{C-N})\text{adj-R2} (12) + \text{R2-puck}(\text{PM3})$
1320	1311	1323(s)	$\nu(\text{C-N})\text{adj-R2} (37) + \nu(\text{C-C})\text{R2} (66) + \text{R5-defor}(\text{PM3})$
1253	1247	1258(vs)	$\nu(\text{C-C})\text{R} (83) + \phi(\text{C-C-C})\text{R} (10) + \nu(\text{C-N})\text{adj-R2}(\text{PM3})$
1233	1228	1229(vs)	$\nu(\text{C-O})\text{adj-Sb} (35) + \nu(\text{C-C})\text{R} (52) + \nu(\text{C-N})\text{adj-R2}(\text{PM3}) + \phi(\text{C-C-H})\text{R5}(\text{PM3}) + \nu(\text{C-C})\text{R2-sym}(\text{PM3})$
1163	1167	1163(s)	$\nu(\text{C-C})\text{R2} (90) + \phi(\text{C-C-C})\text{R2} (11) + \nu(\text{C-N})\text{adjSbR2}(\text{PM3}) + \text{R2-Rock}(\text{PM3})$
1113	1120	1120(w)	$\nu(\text{C-N})\text{adj-R-Sb} (27) + \nu(\text{C-C})\text{R4-asym} (60) + \nu(\text{C-C})\text{-out-of-R} (12) + \phi(\text{C-C-H})\text{R5}(\text{PM3})$
1067	1074	1064(w)	$\nu(\text{C-N})\text{adj-Sb-R2} (32) + \nu(\text{C-C})\text{R2} (51) + \nu(\text{C-C})\text{-out-of-R} (23) + \text{R2-puck}(\text{PM3}) + \nu(\text{C-N})\text{adj-Sb-R2}(\text{PM3})$
1022	1005	1012(w)	$\nu(\text{C-C})\text{R2} (90) + \nu(\text{C-F}) (10) + \nu(\text{C-N})\text{adj-R2}(\text{PM3}) + \phi(\text{C-C-C})\text{R2}(\text{PM3})$
905	909	913(w)	$\nu(\text{C-C})\text{R1} (73) + \nu(\text{C-F}) (10) + \text{R1\&R2-twis}(\text{PM3}) + \phi(\text{C-C-H})\text{R5}(\text{PM3})$
864	875	872(w)	$\nu(\text{C-O})\text{adj-Sb} (43) + \nu(\text{Sb-O}) (14) + \nu(\text{C=O}) (11) + \text{R5-defor}(\text{PM3}) + \nu(\text{C-F})\text{R5}(\text{PM3}) + \nu(\text{Sb-C})\text{R5}(\text{PM3})$
826	822	826(s)	$\nu(\text{C-F}) (30) + \nu(\text{C-C})\text{R4} (36) + \nu(\text{C-C})\text{-out-of-R2} (10) + (\text{C-C-H})\text{-sciss}(\text{PM3})$
753	746	752(s)	$\nu(\text{C-C})\text{-out-of-R} (27) + \tau(\text{C-C})\text{R1} (45) + \nu(\text{C-N}) (10) + \phi(\text{C-C-N}) (10) + \text{R1\&R2-twis}(\text{PM3}) + (\text{C-N-C})\text{R2-wag}(\text{PM3})$
689	656	694(s)	$\phi(\text{C-C-C})\text{R} (57) + \nu(\text{C-C})\text{R} (36) + \text{R5-twis}(\text{PM3}) + \text{R5-wag}(\text{PM3}) + \phi(\text{O=C-C})\text{adj-R2}(\text{PM3}) + \nu(\text{Sb-O})\text{R5}(\text{PM3})$
636	629	627(m)	$\nu(\text{Sb-O}) (37) + \nu(\text{C-C})\text{-out-of-R} (13) + \nu(\text{C-N}) (17) + \phi(\text{C-C-O}) (11) + \phi(\text{O-C=O}) (10) + \text{R2-defor}(\text{PM3}) + \phi(\text{O=C-C})\text{adj-R2-sciss}(\text{PM3})$
594	591	589(s)	$\phi(\text{C-C-F})\text{R3} (43) + \nu(\text{C-C})\text{R3} (10) + \omega(\text{C-F}) (15) + \text{R3-puck}(\text{PM3}) + \text{R4-sciss}(\text{PM3}) + \phi(\text{O=C-C})\text{adj-R2}(\text{PM3})$
520	502	510(s)	$\phi(\text{C-C-C})\text{R4} (76) + \nu(\text{C-C})\text{R4} (10) + \phi(\text{C-C-F})\text{R4}(\text{PM3})$
429	419	426(m)	$\nu(\text{Sb-C}) (23) + \nu(\text{C-C})\text{R-adj-Sb} (10) + \nu(\text{Sb-O})\text{R5}(\text{PM3}) + \text{R1-twis}$
375	368	-	$\nu(\text{Sb-C}) (22) + \nu(\text{Sb-O}) (17) + \phi(\text{C-Sb-C}) (12) + \text{R1,R2\&R3-twis}(\text{PM3})$
282	278	-	$\nu(\text{Sb-C}) (23) (\&\text{PM3}) + \phi(\text{C-Sb-C}) (20) + \phi(\text{C-C-F}) (19) (\&\text{PM3})$

w – weak; vs – very strong; s – strong; m – middle; sh – shoulder; tors – torsion; wag – wagging; defor – deformation; sym – symmetric; asym – antisymmetric; puck – puckering; rock – rocking; twis – twisting; sciss – scissoring, adj – adjacent; and R1, R2 etc. – ring 1, ring 2 etc.

Here we discuss only the conformationally important frequency modes and they are presented in table 1.

The calculated values from PM3 method of the asymmetric vibration of the  $\nu(\text{N-H})$  mode appear at 3285 and 3283 cm<sup>-1</sup> and are observed at 3427 and 3395 cm<sup>-1</sup> respectively. The calculated values from PM3 method of  $\nu(\text{C-H})$  mode vibrations

at 3006, 3000, 2918 and 2997  $\text{cm}^{-1}$  are in accordance with the observed frequencies as shown in table 1.

In the FT-IR spectra a highly intense peak is observed at 1652  $\text{cm}^{-1}$  and it is calculated at 1660  $\text{cm}^{-1}$  with the mode of vibrations as  $\nu(\text{C}=\text{O})$  (64%) PED,  $\nu(\text{C}-\text{O})\text{adj-Sb}$  (20%) and  $\nu(\text{C}-\text{C})\text{-out-of-R}$  (14%). The stretching mode  $\nu(\text{C}=\text{O})$  is reported in the range 1620–1660  $\text{cm}^{-1}$  [17,21,22]. A very sharp absorption peak is observed at 1229  $\text{cm}^{-1}$  which is calculated at 1233  $\text{cm}^{-1}$  with modes of vibrations as  $\nu(\text{C}-\text{O})\text{adj-Sb}$  (35%),  $\nu(\text{C}-\text{C})\text{R}$  (52%) and  $\phi(\text{C}-\text{C}-\text{C})\text{R}$  (10%). This mode is reported in the range 1240–1000  $\text{cm}^{-1}$  in [21,22] and at 1280  $\text{cm}^{-1}$  in [23], which suggests the participation of oxygen in C–O–Sb bonding [23,24]. A strong peak is observed at 826  $\text{cm}^{-1}$  which is calculated at 826  $\text{cm}^{-1}$  having vibrational modes as  $\nu(\text{C}-\text{F})$  (30%),  $\nu(\text{C}-\text{C})\text{R-adj-Sb}$  (36%) and  $\nu(\text{C}-\text{C})\text{-out-of-R}$  (10%). This vibrational mode  $\nu(\text{C}-\text{F})$  is in very good agreement with the mode reported in [25,26], which is in the frequency range 824–859  $\text{cm}^{-1}$  and in the range 780–680  $\text{cm}^{-1}$  in [20]. A medium intensity absorption peak is observed in the FT-IR spectra at 627  $\text{cm}^{-1}$  and is calculated at 636  $\text{cm}^{-1}$  with vibrational modes  $\nu(\text{Sb}-\text{O})$  (37%),  $\nu(\text{C}-\text{C})\text{-out-of-R}$  (13%),  $\nu(\text{C}-\text{N})\text{R}$  (18%),  $\phi(\text{C}-\text{C}-\text{O})$  (11%) and  $\phi(\text{O}-\text{C}=\text{O})$  (10%). The stretching vibration  $\nu(\text{Sb}-\text{O})$  is reported in the range 561–585  $\text{cm}^{-1}$  by Khosa *et al* [27] and at 755  $\text{cm}^{-1}$  by Shankar *et al* [28]. So this mode exists in between these two reported modes which appears to be the characteristic mode of the title compound. A peak of medium intensity is observed at 589  $\text{cm}^{-1}$  and it is calculated at 594  $\text{cm}^{-1}$ , with vibrational modes as  $\phi(\text{C}-\text{C}-\text{F})$  (43%),  $\omega(\text{C}-\text{F})$  (15%) and  $\nu(\text{C}-\text{C})\text{R-adj-Sb}$  (6%). This mode of  $\phi(\text{C}-\text{C}-\text{F})$  is reported at 427  $\text{cm}^{-1}$  in [25], and hence there is a slight deviation in the value of frequency for this mode. This is probably due to the different positions of fluorine atoms in the present compound and presence of nitrogen atoms as well. In the FT-IR spectra a highly intense absorption peak is observed at 510  $\text{cm}^{-1}$  which is calculated at 520  $\text{cm}^{-1}$  having vibrational modes  $\phi(\text{C}-\text{C}-\text{C})\text{R}$  (76%) and  $\nu(\text{C}-\text{C})\text{R}$  (10%). This mode is in accordance with that reported in [25,29] which is in the range 518–520  $\text{cm}^{-1}$ . A medium intensity peak is observed at 426  $\text{cm}^{-1}$  in the spectra and it is calculated at 429  $\text{cm}^{-1}$ , with modes of vibrations as  $\nu(\text{Sb}-\text{C})$  (23%),  $\nu(\text{C}-\text{C})\text{R}$  (10%). The mode  $\nu(\text{Sb}-\text{C})$  is reported in the frequency range 459–484  $\text{cm}^{-1}$  by Khosa *et al* [27] and in the range 449–477  $\text{cm}^{-1}$  by Shankar *et al* [28]. Thus current mode is slightly less than that reported by Khosa and Shankar and so this mode may be a find for the title compound. Another mode is the  $\nu(\text{Sb}-\text{O})$  calculated by the PM3 method at 419  $\text{cm}^{-1}$  [30].

## 5. Conclusions

The vibrational dynamics of this compound show close resemblance of calculated and observed vibrational bands. The title compound shows low value of  $\Delta\nu(\text{CO}_2)$  (i.e. from table 1,  $\nu_{\text{asym}} - \nu_{\text{sym}}$ ) which is equal to 1652–1229 = 423  $\text{cm}^{-1}$ . This clearly indicates that there will be at least moderate if not strong interaction between carbonyl oxygen atom of the carboxylate group and the central antimony atom with the valency equal to seven including secondary bonding interactions.

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## References

- [1] K Hartke and H M Wolff, *Chem. Ber.* **113**, 1394 (1980)
- [2] P L Millington and D B Sowerby, *J. Chem. Soc. Dalton Trans.* **1199** (1992)
- [3] M Dogamala, F Huber and H Preut, *Z. Anorg Allg. Chem.* **571**, 130 (1989)
- [4] Y Q Ma, J S Li, Z N Xuan and R C Liu, *J. Organomet. Chem.* **620**, 235 (2001)
- [5] K Singhal, R Rastogi and P Raj, *Indian J. Chem.* **A26**, 146 (1987)
- [6] A Glowacki, F Huber and H Preut, *Recl. Trav. Chim. Pays-Bas.* **107**, 278 (1988)
- [7] L Yu, Y Q Ma, G C Wang and J S Li, *Heteroatom Chem.* **15**, 32 (2004)
- [8] E B Wilson Jr., J C Decius and P C Cross, *Molecular vibrations* (Dover Publications, New York, 1980) pp. 11–31
- [9] H C Urey and C A Bradley, *Phys. Rev.* **38**, 1969 (1931)
- [10] Cambridge Crystallographic Data Centre, CCDC No. 211365
- [11] T Shimanouchi, in: *Computer program for normal coordinate treatment of polyatomic molecules* (University of Tokyo, 1968)
- [12] T Hasan, P K Singh, R Misra, P Raj and N Misra, *Pramana – J. Phys.* **68(5)**, 875 (2007)
- [13] S Srivastava, S Srivastava, S Singh, V P Gupta and V D Gupta, *Eur. Polym. J.* **38(7)**, 1423 (2002)
- [14] H J Gotze, P Lemannzich and B Schaaf, *Spectrochim. Acta Part A* **50**, 1871 (1994)
- [15] J R Scherer, *Spectrochim. Acta* **20**, 345 (1964)
- [16] M Tasumi, T Urano and M Nakata, *J. Mol. Structure* **146**, 383 (1986)
- [17] C L Lau and R G Snyder, *Spectrochim. Acta Part A* **27**, 2073 (1971)
- [18] N Misra, O Prasad and L Sinha, *Indian J. Biochem. Biophys.* **43**, 173 (2006)
- [19] P K Singh, T Hasan, O Prasad, L Sinha, K Raj and N Misra, *Spectroscopy* **20(5–6)**, 275 (2006)
- [20] J J P Stewart, MOPAC 2007, Stewart Computational Chemistry, version 7.075W
- [21] N B Colthup, L H Daly and S E Wiberley, *Introduction to infrared and Raman spectroscopy* (Academic Press, New York, 1964) p.74  
N B Colthup, L H Daly and S E Wiberley, *Introduction to infrared and Raman spectroscopy* (Academic Press, New York, 1964) p. 199,212,225,249,314,315
- [22] T Ilani, E Shultz and B Chefetz, *J. Environ. Qual.* **34**, 552 (2005)
- [23] N S Biradar and V K Kulkarni, *J. Inorg. Nucl. Chem.* **33**, 3781 (1971)
- [24] J N R Ruddick and J R Sames, *J. Organometal. Chem.* **60**, 233 (1973)
- [25] K Shobatake, C Postmus, J R Ferraro and K Nakamoto, *Appl. Spectrosc.* **23(1)**, 12 (1969)
- [26] G M W Kroesen, H J Lee, H Moriguchi, H Motomura, T Shirafuji and K Tachibana, *J. Vac. Sci. Technol.* **A16(1)**, 225 (1998)
- [27] M K Khosa, M Mazhar, S Ali, K Shahid and F Malik, *Turk. J. Chem.* **30**, 345 (2006)
- [28] D Shankar, A R Rai, Y P Singh, H Rehwani, V Khushalani and R S Gupta, *Bioorgan. Chem. Appl.* **2006**, 1 (2006)
- [29] J A Ciezak and J B Leao, *J. Phys. Chem.* **A110**, 3759 (2006)
- [30] P Raj, S Agnihotri and K Singhal, *Syn. Reactivity in Inorg. Metal-Org. Nano-metal Chem.* **32**, 569 (2002)